Project ID: FC146

Advanced Materials for Fully-Integrated MEAs in AEMFCs

PI: Yu Seung Kim

Los Alamos National Laboratory

June 15, 2018

Overview

Timeline

- Project start date: 11/2/2015
- Project end date: 11/2/2018
- Percent complete: 85%

Budget

- Total project funding: $3,060K
  - DOE share: 98%
  - Contractor share: 2%
- Funding received in FY18: $980K
- Total DOE Funds Spent*: $2,390K

*As of 4/17/2018

Barriers

- B. Cost
- C. Electrode performance
- A. Durability

Project lead

- Los Alamos National Laboratory
  Yu Seung Kim (PI) , Sandip Maurya, Eun Joo Park, Dongguo Li, Ivana Matanovic

Partners

- Sandia National Laboratories
  Cy Fujimoto (Co-PI), Michael Hibbs
- Rensselaer Polytechnic Institute
  Chulsung Bae (Co-PI), Sangtak Noh, Jongyeob Jeon, Junyoung Han
- Argonne National Laboratory
  Vojislav Stamenkovic, Rongyue Wang

Relevance

Objective

- Development of improved AEMs, ionomeric binders and integration of catalysts and AEMs into high-performance MEAs.

Technical Target

	Units	LANL Baseline (2015)	DOE Target[1] (4Q, 2017)	Current Status (1Q, 2018)
ASR	Ω/cm^2	0.2	≤ 0.1	**0.05[2]**
AEMFC Performance	mA/cm^2 at 0.6 V	420 (382 kPa)[1]	600 (≤ 152 kPa) atm)	**950 (78 kPa)[2]**
AEM Durability	ASR after 500 h run at 600 mA/cm^2	0.8 after 300 h run at 0.3 V	< 0.1	**0.05[3]**
AEMFC Durability	% V loss after 2000 h at 0.6 A/cm^2 at ≥ 60°C	60% after 300 h run at 0.3 V at 60°C[3]	< 10% (2Q, 2019)	12.5% V loss at 0.6 A/cm^2 after 500 h at 80°C[3]

[1]From FCTO MYRDD Plan; [2]Technical Back-up Slide #1; [3]Slide 7

Approach

Research Focus	Major Founding	Breakthrough
AEM **Stability** (2016)	**Polymer backbone degradation via aryl-ether cleavage**[1]	**Aryl-ether free polyaromatics:** *Demonstrated > 2000 h stability in 4 M NaOH 80 ℃*
AEMFC **Performance** (2017)	**Phenyl group adsorption**[2]	**Poly(fluorene) ionomers:** *Demonstrated 1.5 W/cm^2 peak power density*
AEMFC **Durability** (2018)	*In progress*	*Not yet*

[1]Fujimoto et al. *J. Memb. Sci.* 423-424, 438-449, 2012; [2]Matanovic et al. *J. Phy. Chem. Let*. 8, 4918-4924, 2016

Milestone & go-no-go decision

Date	Milestone & Go-No-Go	Status# (%)	Result	Comments
Mar. 2016	Down-select AEM	100 (Feb. 2016)	Poly(phenylene)	Poly(terphenylene) (RPI) & Diels Alder poly(phenylene) (SNL)
Dec. 2016	Down-select ionomer	100 (June 2017)	Poly(fluorene)	6 month delayed due to incomplete HOR study
Mar. 2017	*In-situ* AEM ASR $\leq 0.1\ \Omega\ cm^2$ for 500 h at 600 mA/cm^2 (Go-No Go)	100 (Mar 2018)	**$0.05\ \Omega\ cm^2$**	Completed *ex-situ* test on Dec. 2016; postponed *in-situ* test due to delay of the down-selection of ionomer and HOR catalyst
Jun. 2017	Assess perfluorinated ionomer property	100 (Mar. 2017)	Stable for 120 h at 0.5 M NaOH, 80°C	Stop further development by reviewers' suggestion
SEP. 2017	Integrate MEAs; Peak power density > 0.6 W/cm^2	100 (Apr. 2017)	**1 W/cm^2**	Best AEMFC performance using polyaromatic ionomer by the time
Dec. 2017	Down-select HOR catalyst	100 (Oct. 2017)	PtRu/C	Least phenyl group adsorbing catalyst
Mar. 2018	Integrate MEAs; Peak power density: 1 W/cm^2	100 (Dec. 2018)	**1.5 $W/\ cm^2$**	Best AEMFC performance using polyaromatic ionomer by the time
July. 2018	< 10% V loss for 2000 h	25	12.5% for 500 h	Completed 500 h test (3/2018)
Sep. 2018	Deliver 50 cm^2 MEAs	10		

Red: delayed; Blue: exceed milestone criteria

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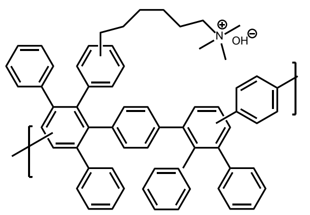
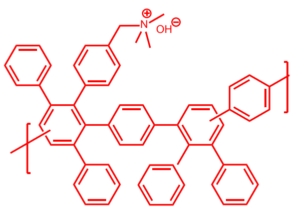
Ex-situ alkaline stability of the down-selected AEM

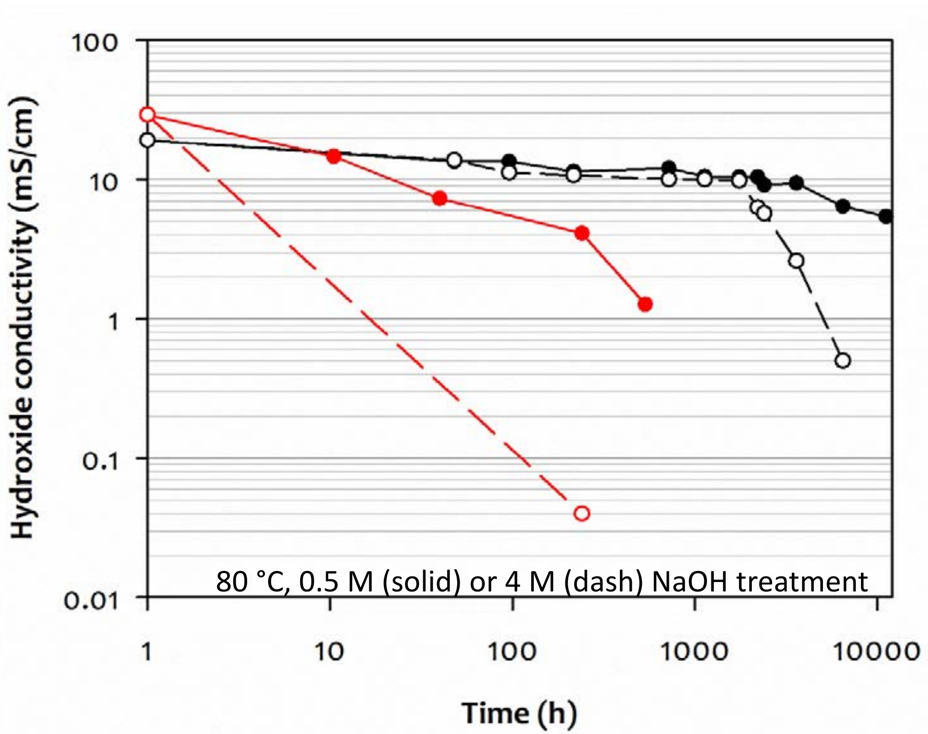
AEM stability test: Immerse AEMs in 0.5 M or 4 M NaOH at 80°C. Conductivity measured at 30°C/95% RH during the stability test.



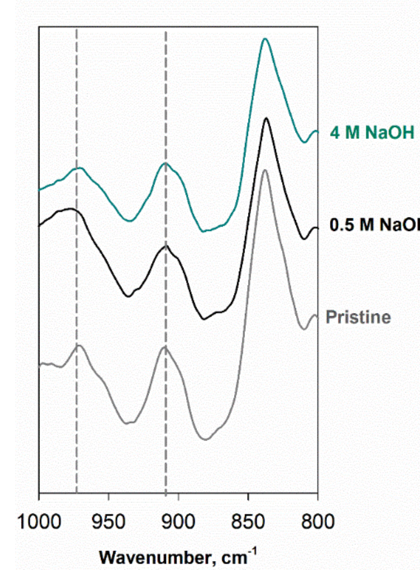
Down-selected PP-HTMA



ATM-PP (control)



FTIR of PP-HTMA after 3600 h NaOH treatment



- Completed 11,000 h AEM stability test
- Highlight: No conductivity & structural changes for the down-selected AEM after 4 M NaOH treatment at 80°C for 2,200 h. → Known most-alkaline stable AEM

More info for PP-HTMA: see Technical Back-up Slide #2

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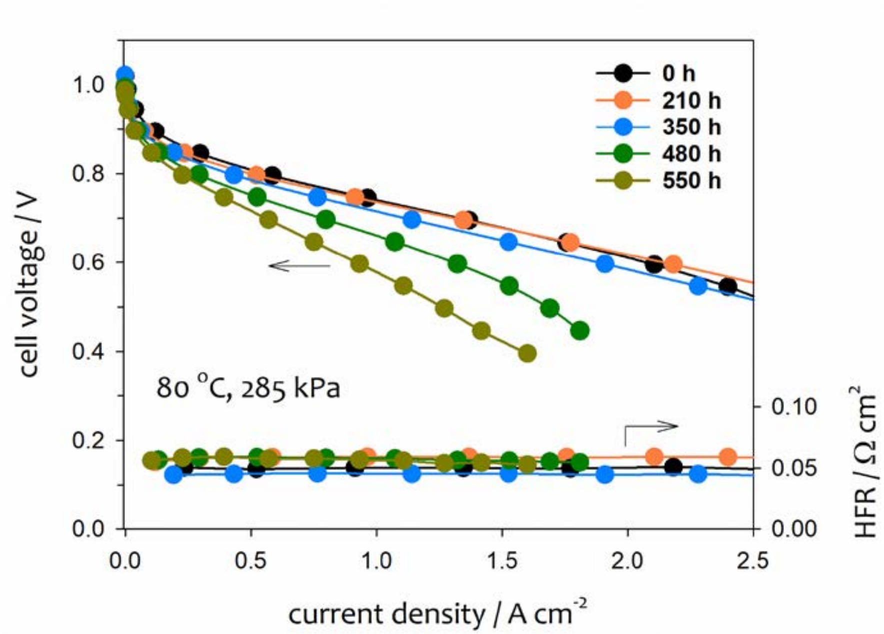
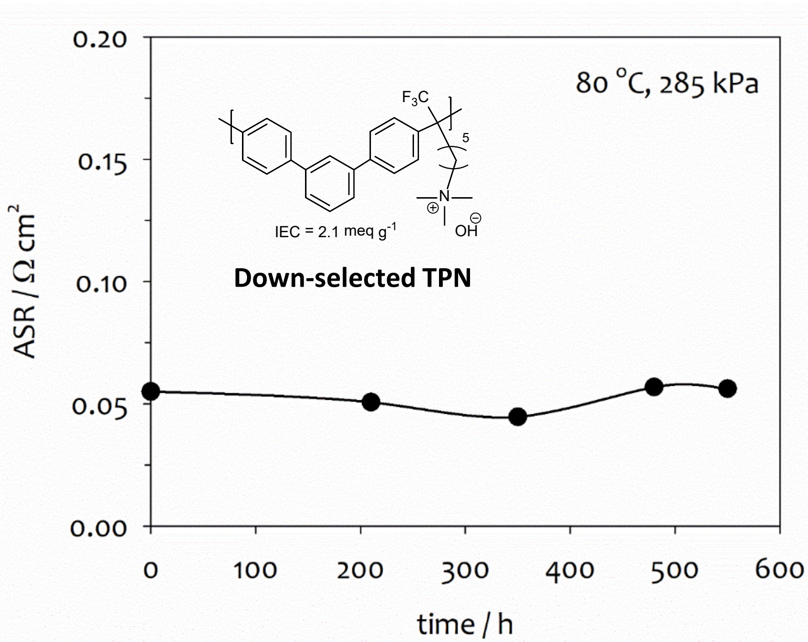
In-situ alkaline stability of the down-selected AEM

AEM: Down-selected poly(terphenylene) (TPN) (thickness: 40 μm), **Ionomer:** poly(fluorene) (FLN), **Catalyst:** Pt-Ru/C 0.5 mg_{Pt}/cm^2 (anode), Pt/C 0.6 mg_{Pt}/cm^2 (cathode).

Life test: Operating AEMFC under H_2/O_2 conditions, 146 kPa backpressure at constant current density (0.6 A/cm^2)



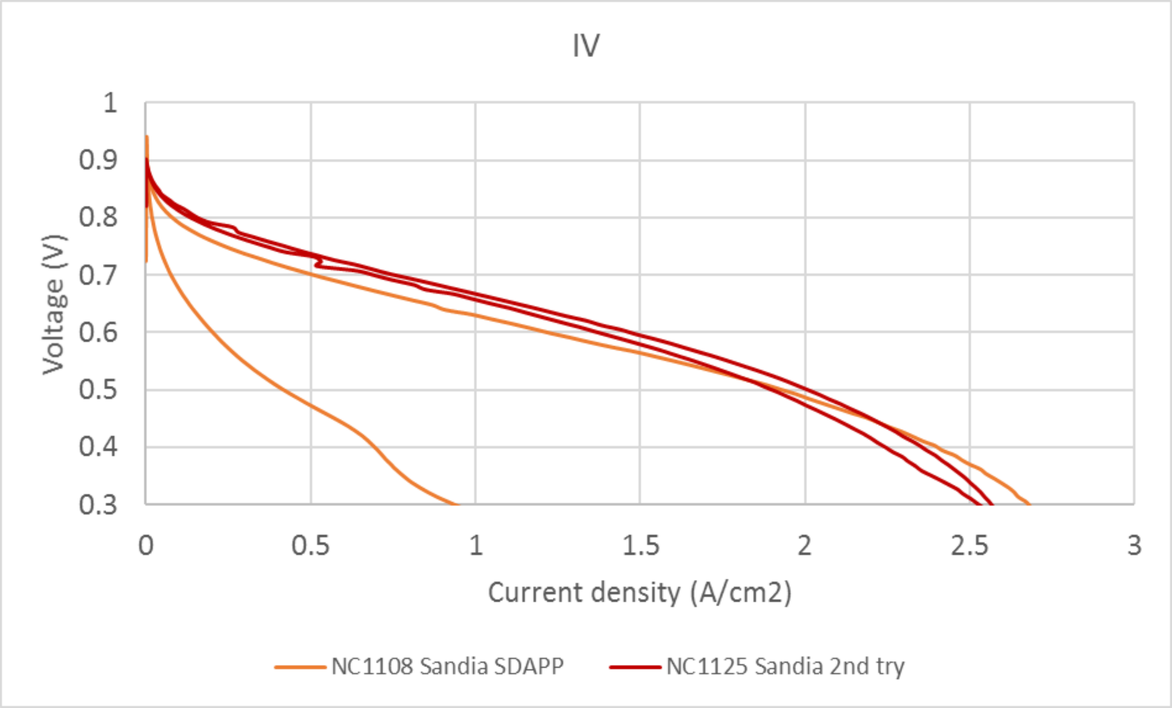


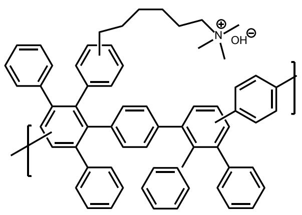
- Highlight: No HFR change during 550 h life test; The ASR = ~0.05 Ω cm^2 met Go-No-Go decision criteria (*In-situ* AEM ASR ≤ 0.1 Ω cm^2 for 500 h at 0.6 mA/cm^2)

More info for TPN: see Technical Back-up Slide #2

Performance verification of the down-selected AEM

AEM: Down-selected PP-HTMA, **Ionomer and catalysts:** Pocelltech standard; measured under H_2/CO_2-free air





Down-selected PP-HTMA

HFR: 0.073Ω·cm²

OCV: 0.9V

Peak Power density: 1 W/cm²

- Pocelltech verified AEM ASR. HFR value of the cell (0.073 Ω cm²) is in good agreement with LANL data.

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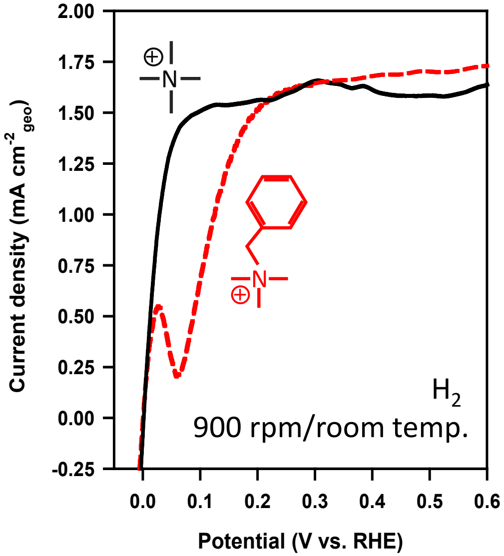
POCELLTECH

Identify AEMFC performance limiting factor

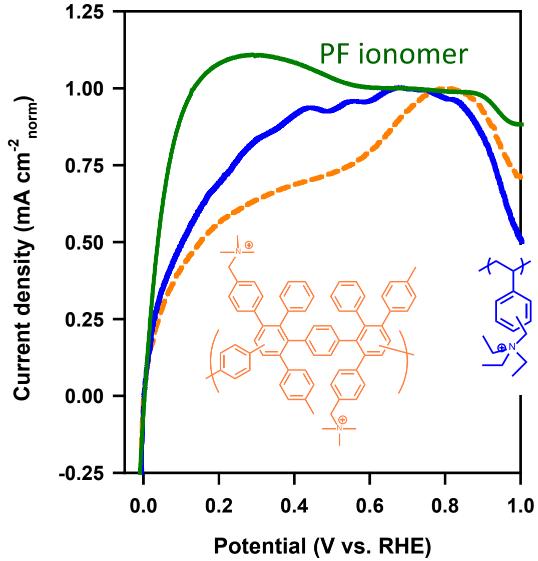
Pt RDE experiment

in tetramethylammonium &
benzyltrimethylammonium



Phenyl adsorption may inhibit HOR activity

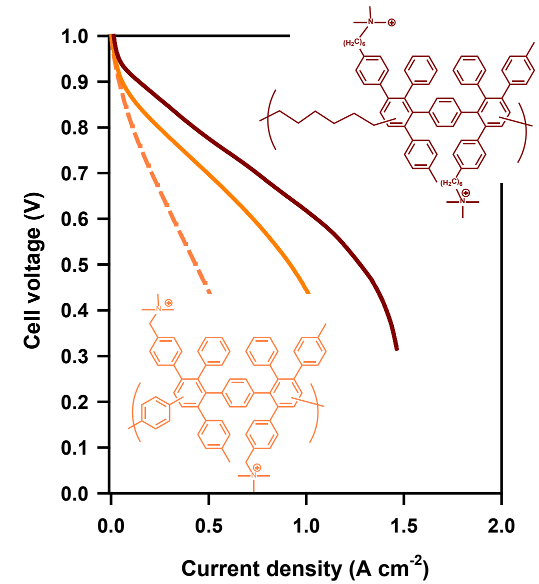
Ionomer coated Pt microelectrode experiment



Better HOR activity with less phenyl group containing ionomer

Fuel cell test

Solid line: Pt-Ru/C anode
Dash line: Pt/C anode



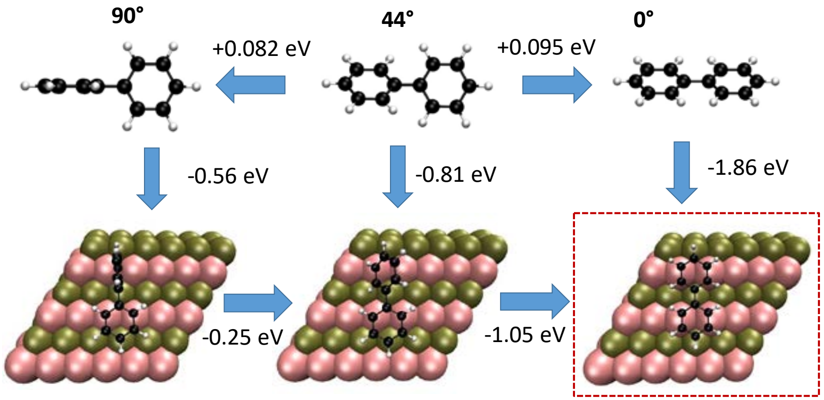
Better HOR activity with less phenyl group ionomer + Pt-Ru

- **Phenyl group adsorption** is the AEMFC performance limiting factor

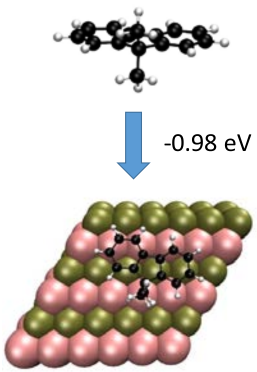
DFT adsorption energy of phenyl group: see Technical Back-up Slide #3

HOR ionomer development and down-selection

Biphenyl adsorption on Pt-Ru



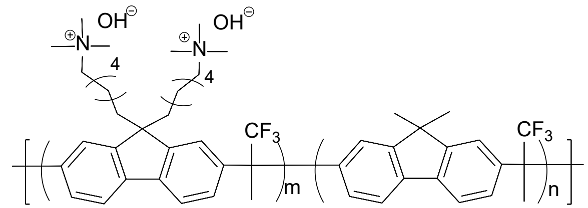
Fluorene adsorption on Pt-Ru



Significant biphenyl adsorption on Pt-Ru (E_{ads} = 0.98 eV) due to phenyl ring rotation while the adsorption of phenyl group in fluorene is minimal.

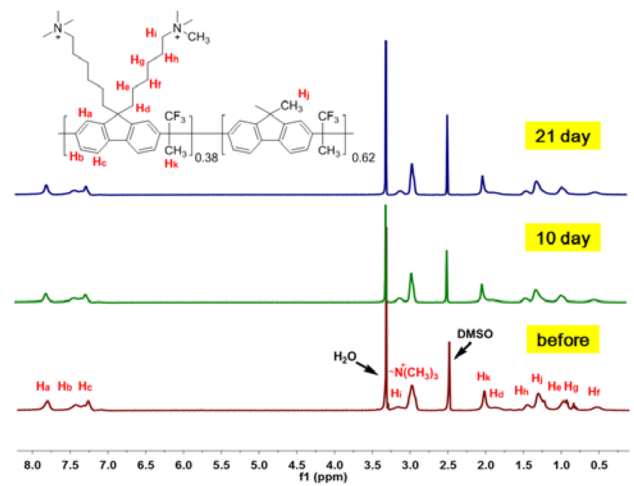
More info: Back-up slide #3

Poly(fluorene)s



Detailed synthetic procedure: see Back-up Slide #4

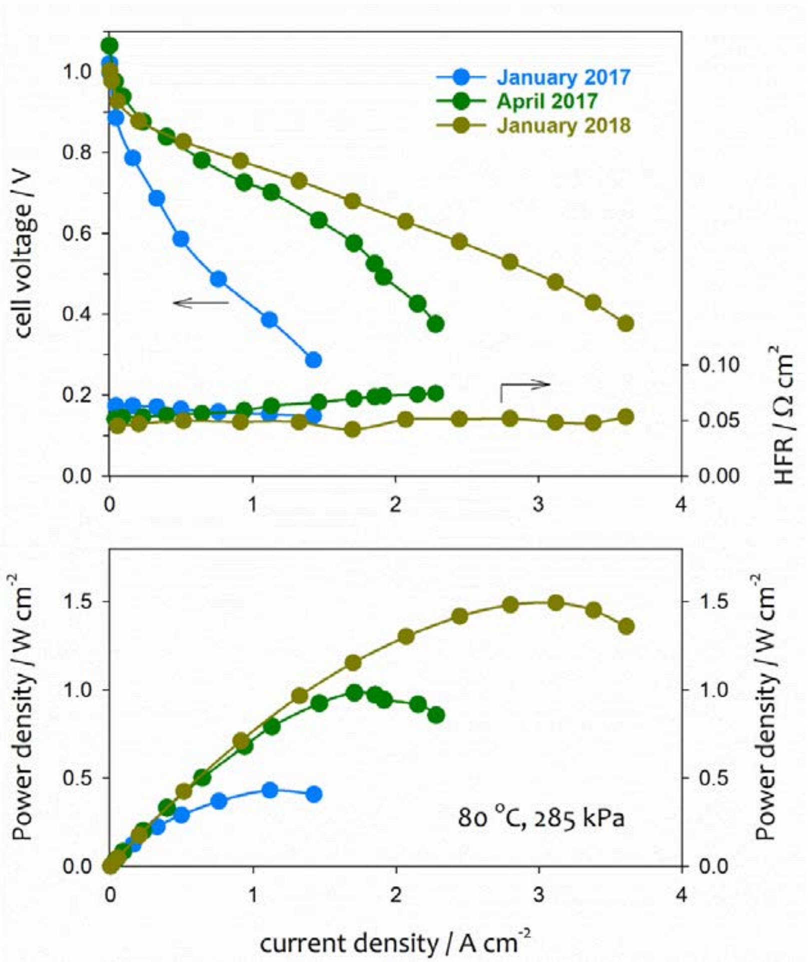
Alkaline stability (1M NaOH, 80°C)



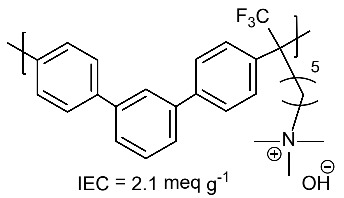
- Highlight: Poly(fluorene) ionomer was down selected based on DFT result (E_{ads} = 0.98 eV).

AEMFC performance using project down-selected materials

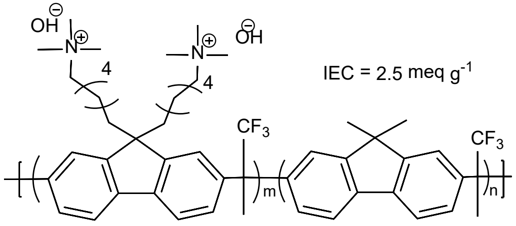
AEM: TPN (thickness: 35 μm), **Ionomer:** FLN, **Catalyst:** Pt-Ru/C 0.5 mg_{Pt}/cm^2 (anode), Pt/C 0.6 mg_{Pt}/cm^2 (cathode). Measured under H_2/O_2 condition



Down-selected AEM Poly(terphenylene) (TPN)



Down-selected ionomer Poly(fluorene) (FLN)

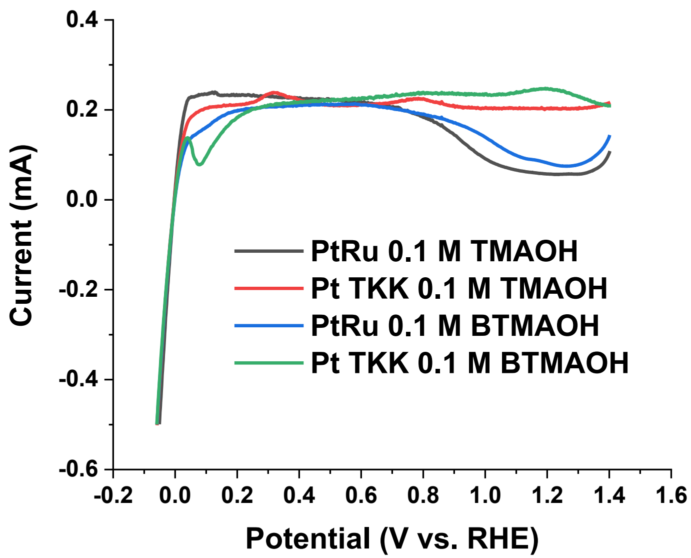


- Highlight: Achieved 1.5 W/cm^2 peak power density with down-selected AEM and ionomer (exceed milestone criteria and best-known performance using polyaromatic AEM and ionomer).

For H_2/air data and low backpressure performance, see Technical back-up slide #1

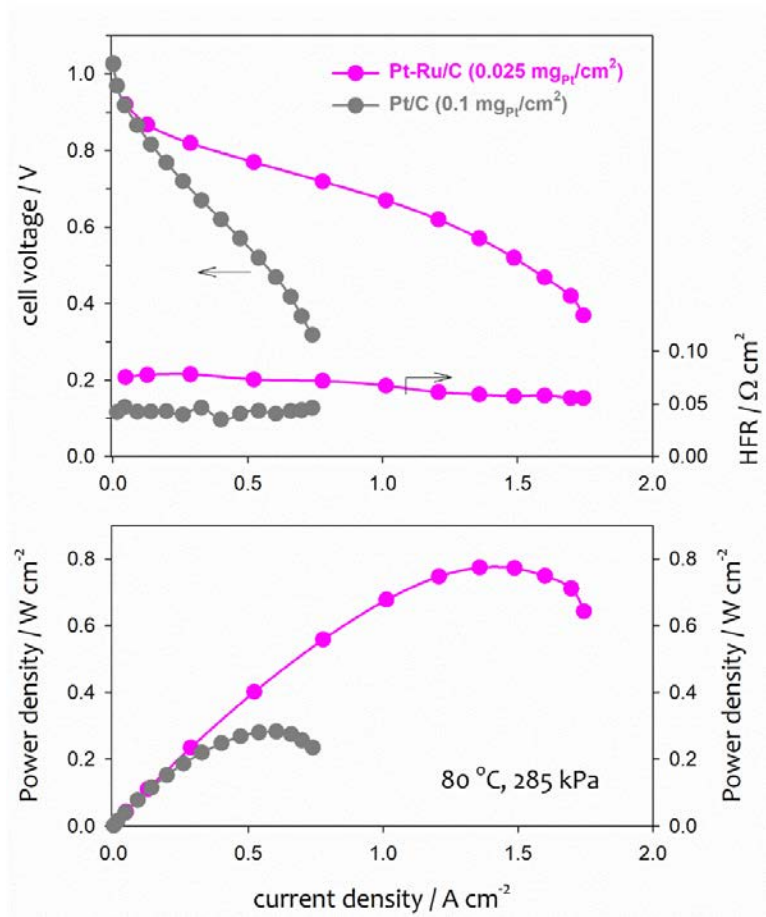
Low Pt-loading anode catalyst

HOR voltammogram of Pt/C (ANL) and Pt-Ru/C (TKK) in 0.1 M TMAOH and BTMAOH



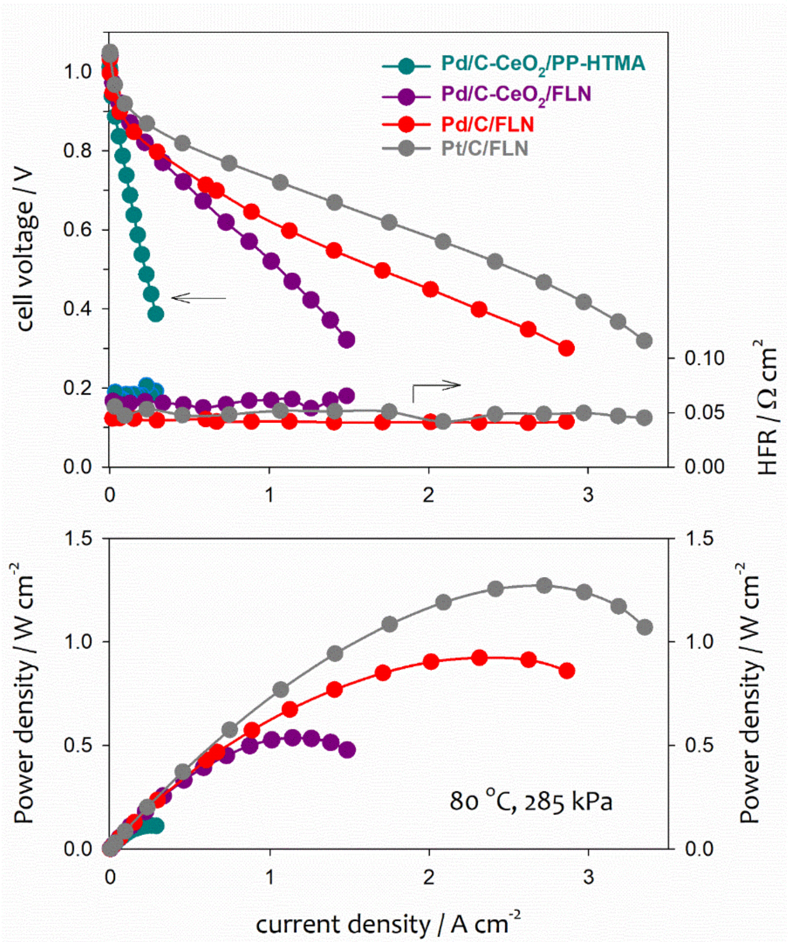
- The Pt-Ru/C HOR catalyst (ANL) exhibited much higher HOR activity due to less-phenyl group adsorption.
- Highlight: Achieved 800 mW/cm^2 peak power density with 0.025 mg$_{Pt}$/cm^2.

AEM: TPN (thickness: 35 μm), **Ionomer:** FLN, **Catalyst:** Pt_1-Ru_8/C 0.1 mg$_{metal}$/cm^2 or Pt/C 0.1 mg$_{Pt}$(anode), Pt/C 0.6 mg$_{Pt}$/cm^2 (cathode). Measured under H_2/O_2 condition

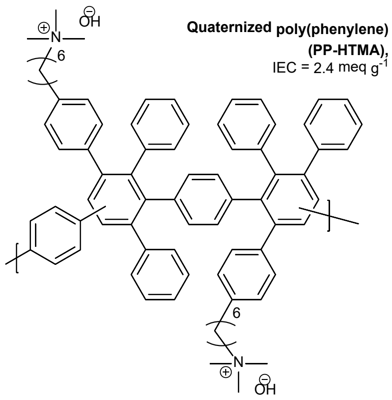


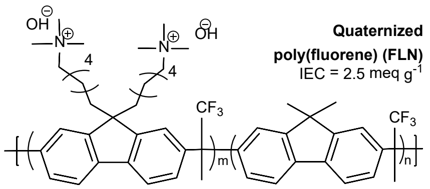
Pd-based (Non-Pt) anode catalysts*

AEM: TPN (thickness: 35 μm), **Ionomer:** FLN or PP-HTMA, **Catalyst:** Pd/C, Pd/C-CeO_2, or Pt/C 0.6 mg_{metal}/cm^2 (anode), Pt/C 0.6 mg_{Pt}/cm^2 (cathode). Measured at H_2/O_2.



Ionomers for the study





- Ionomer impacts the AEMFC performance of Pd-anode catalyzed MEAs
- Maximum power density of 950 mW/cm^2 obtained with Pd/C anode catalyzed AEMFC (~ 75% of the peak power density of Pt catalyzed AEMFC)

* Detailed information for Pd-based catalyst:
see ref. Miller et al. Angewandte Chemie, 2016, 128, 6108-6111

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TECHNION Israel Institute of Technology

Responses to previous year reviewers' comments

- **The project needs to begin considering non-Pt catalysts and the effect of air at some point.**
  We started the non-Pt (non-Pt) catalysts from this year with down-selected materials. We have tested non-PGM HOR and ORR catalysts (shown in Back-up Slide #5). The data is preliminary and we are looking for performance improvement. We started to examine H_2/air performance and report H_2/air performance (Back-up Slide #1).

- **A number of collaborators are listed, but it is not clear that materials have been exchanged with these partners.**
  Material transport is essential. Materials developed from this projects have been provided a number of collaborators. We included some important material test data in this presentation.

- **Better collaboration should be done with other laboratories working on these AEM materials.**
  Some materials developed from this project have sent to NREL and LBNL in addition to our former collaborative national labs (Argonne and Sandia).

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Collaboration and Partners

Project team

Los Alamos National Laboratory · Sandia National Laboratories · Rensselaer · Argonne National Laboratory

Collaboration

POCELLTECH	AEM supply & evaluation (Slide 8)
XERGY	AEM commercialization
NanoSonic (Putting nanotechnology to work)	AEM supply
Berkeley Lab	AEM & ionomer supply
Technion – Israel Institute of Technology	Non-Pt HOR catalyst (Slide 13)
The University of New Mexico	DFT calculation, non-PGM HOR catalyst (Slide 10)
University at Buffalo – The State University of New York	Non-PGM ORR catalyst
Washington State University	Non-PGM ORR catalyst (Back-up Slide #5)
東京工業大学 Tokyo Institute of Technology	Reinforced AEM supply

Small samples were also provided to NREL, University of Arizona and other research institutes

Remaining challenges and barriers

Within the project (ending November 2, 2018)

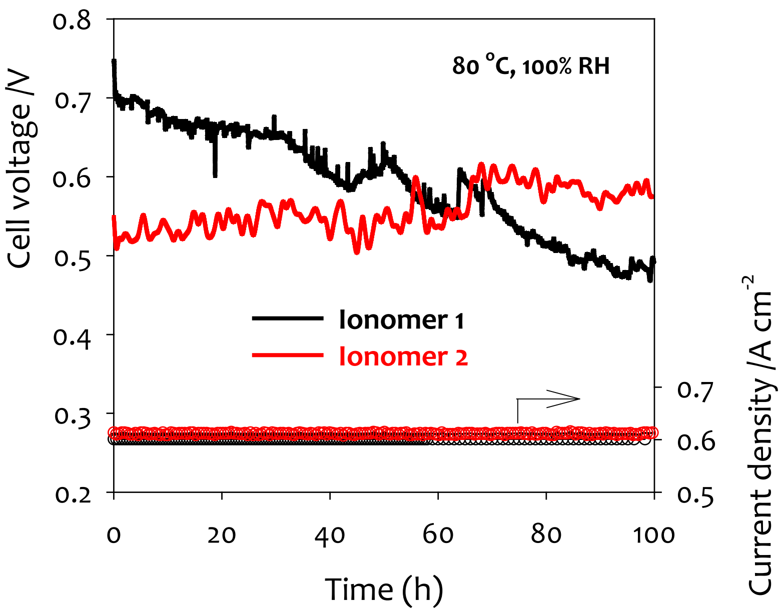
- Durability issue is probably the most urgent remaining challenge and technical barrier for AEMFC technology. LANL team is trying to find the durability limiting factor of AEMFC rest of the project period. Probably continue beyond this project period. Below figure shows some progress.

After the project

- Robust thin membrane production (RPI, Xergy, TIT)
  - PTFE reinforcement
  - Pore-filling membrane

- Integration of non-PGM or low PGM catalysts (LANL, ANL, SUNY Buffalo, WSU, UNM)
  - HOR catalyst
  - ORR catalyst

Short-term AEMFC test



Proposed future work

Remainder of FY 2018 (7 month)

AEM and ionomer synthesis (SNL, RPI, LANL)
- Large scale (> 10 g) down-selected AEM and ionomer synthesis

AEMFC performance (LANL, ANL)
- Complete performance assessment of MEAs employing non-PGM ORR catalysts
- Complete performance assessment of MEAs employing reinforced or ultrathin membranes
- Complete performance assessment of MEAs employing non-PGM HOR catalysts

AEMFC durability (LANL)
- Identify durability limiting factor
- Complete > 500 h life test at a constant current density of 0.6 A/cm^2 & post mortem analysis

Any proposed future work is subject to change based on funding levels.

Technology transfer activities

- **RPI:** established a joint venture to produce large scale production of AEM and ionomers.
- **SNL:** CRADA with an industrial partner.
- **LANL:** Participated in a SBIR program to license AEM technology.

- **FY 2018 patent and patent applications**

- **SNL & LANL:** "Poly(phenylene alkylene)-based ionomers" US 9,534,097 (2017).
- **LANL:** "Polymer electrolytes for alkaline membrane fuel cells" S133606 (March, 2, 2018)

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Summary

Objective: Development of improved AEMs, ionomeric binders and integration of catalysts and membranes into high-performance MEAs.

Relevance: Aiming to make AEMFC system competitive to PEMFCs in terms of performance and durability. Identifying performance barrier and degradation mechanism of AEMFCs.

Approach: Preparing AEMs without aryl-ether free polyaromatics (Year 1). Developing high-performing ionomers through catalyst-ionomer interfacial study (Year 2). Demonstrating AEMFC durability of fully-integrated MEAs from materials developed from this project (Year 3).

Accomplish-ments (FY 17) Completed to prepared AEMs with exceptional stability with desired film forming properties. Demonstrated stable ASR **~ 0.05 Ω cm² for 500 h MEA operation at 0.6 A/cm².** Designed **new fluorene ionomer** that exhibited **1.5 W/cm²** (H_2/O_2) and **680 mW/cm²** (H_2/CO_2-free air) peak power density of AEMFC performance. Implemented non-Pt and low-Pt HOR catalysts in MEAs, which exhibiting promising performance.

Collaborations: Multiple collaborations with academia, industry and other national labs. In most cases, our team has provided alkaline membranes to the collaborators or has obtained potential catalyst materials for MEA testing. Tech transfer efforts have been made with several small business.

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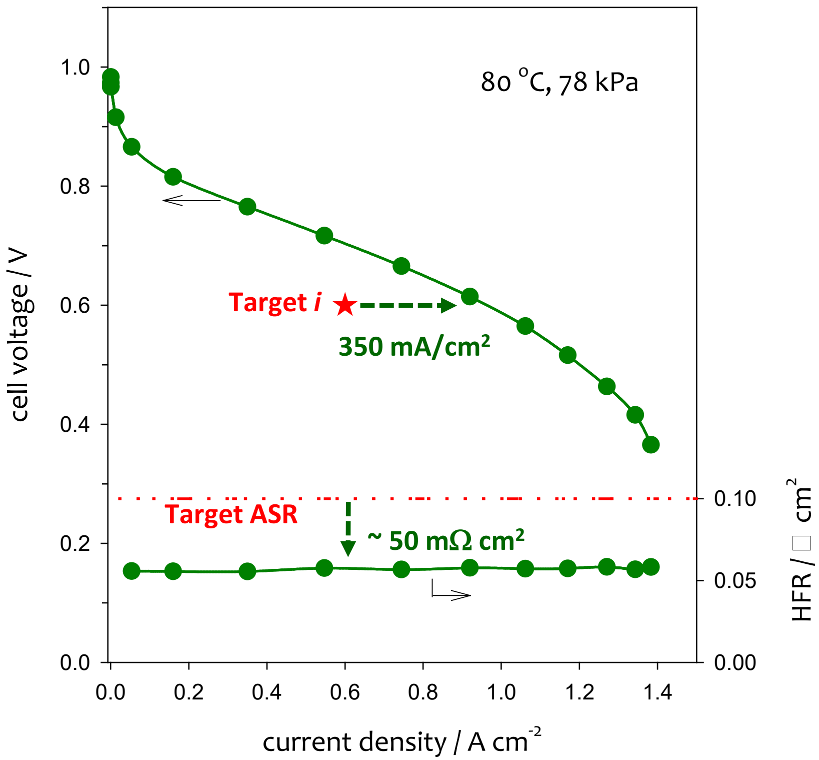
Technical Back-Up Slides

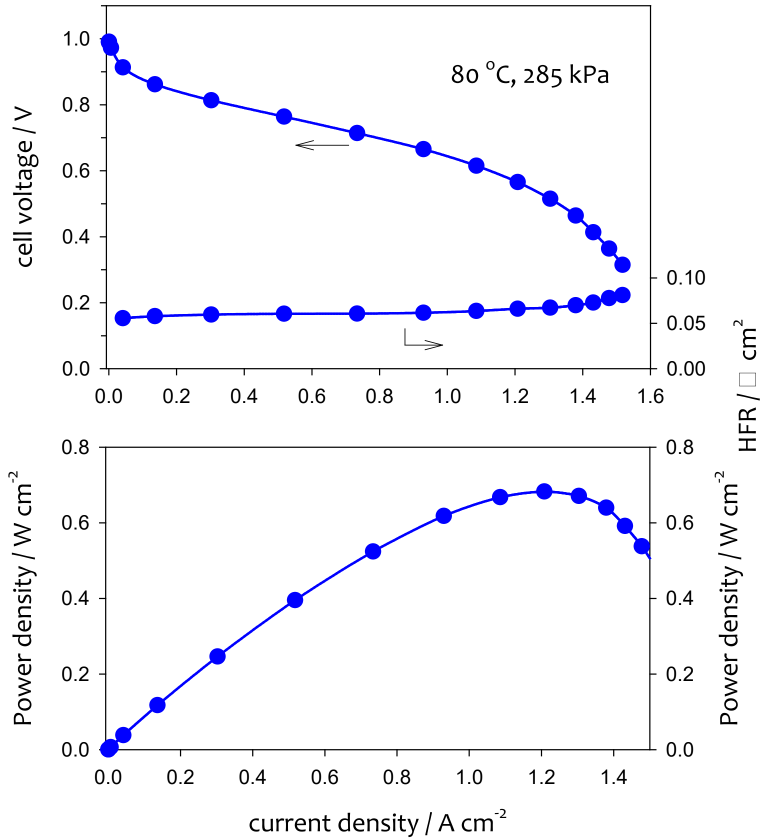
AEMFC performance using the project down-selected materials

AEMFC performance exceeds project target



AEM: TPN (thickness: 35 μm), **Ionomer:** FLN, **Catalyst:** Pt-Ru/C 0.5 mg_{Pt}/cm^2 (anode), Pt/C 0.6 mg_{Pt}/cm^2 (cathode). Measured under H_2/O_2; 78kPa abs backpressure (ambient condition at Los Alamos altitude (7000 ft)

H_2/air AEMFC reaches 0.68 W/cm² peak power



AEM: TPN (thickness: 35 μm), **Ionomer:** FLN, **Catalyst:** Pt-Ru/C 0.5 mg_{Pt}/cm^2 (anode), Pt/C 0.6 mg_{Pt}/cm^2 (cathode). Measured under H_2/CO_2-free air ; 285kPa backpressure

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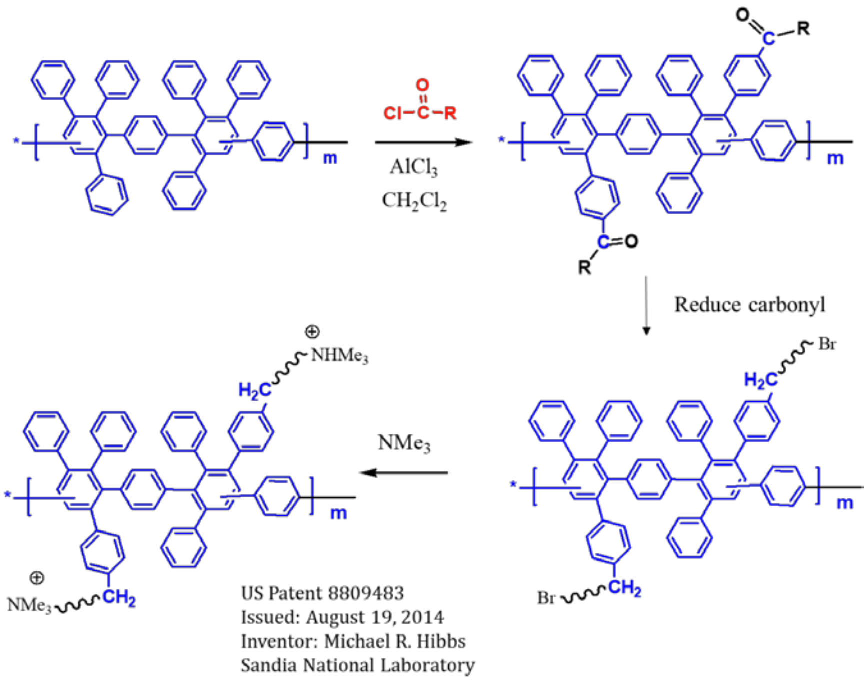
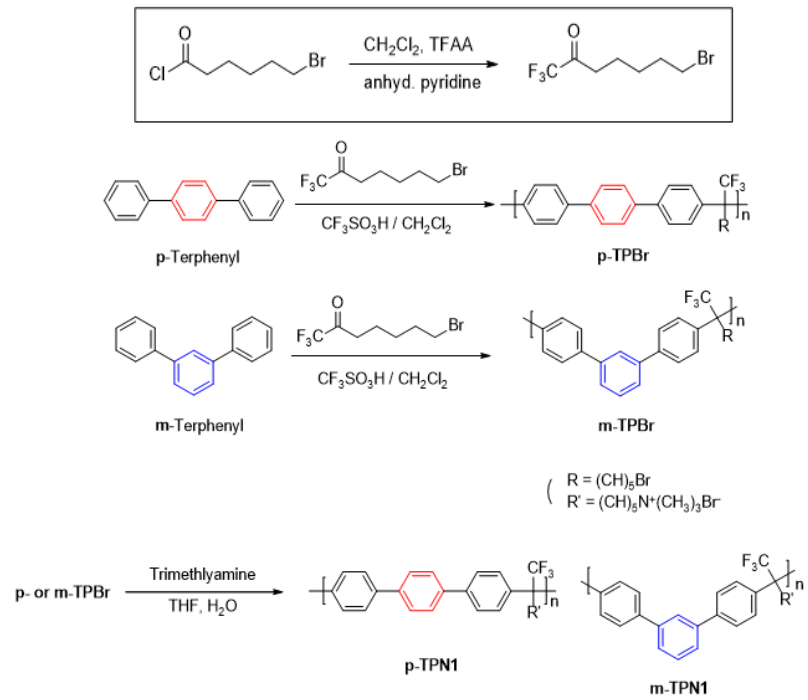
Synthesis of down-selected AEMs (aryl-ether free polyphenylene)s

Alkylammonium functionalized Diels-Alder Poly(phenylene)s (PP-HTMA)



Ref. Hibbs, *J. Polym. Sci. Part B:* 2013, 51, 1736.
Maurya et al. *Chem. Mater.* 2018, 30, 2188.

Alkylammonium functionalized poly(terphenylene)s (TPN)



Ref. Lee at al. *ACS Macro Let.* 2017, 6, 566-570.

- Down-selection was based on hydroxide conductivity and alkaline stability.

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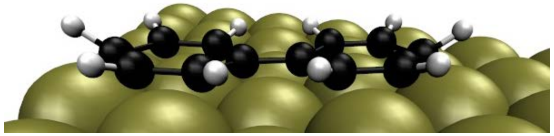
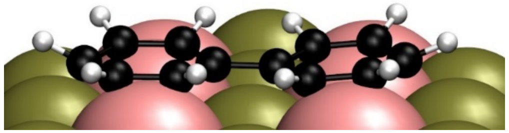
Adsorption energy of phenyl group on Pt and Pt-Ru surface

Biphenyl group on Pt (111)



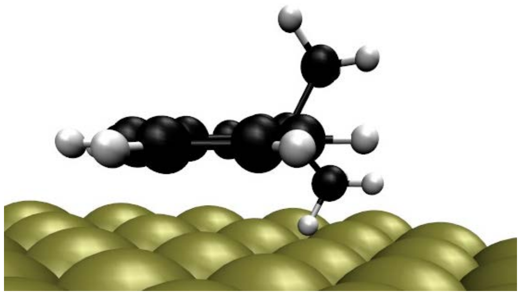
E_{ads}= -2.30 eV

Biphenyl group on Pt-Ru (111)



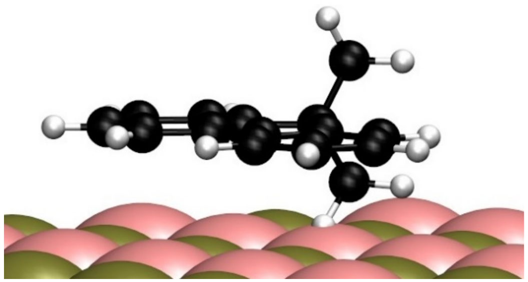
E_{ads}= -1.86 eV

Fluorene on Pt (111)



E_{ads}= -1.06 eV

Fluorene on Pt-Ru(111)



E_{ads}= -0.98 eV

Pt

Adsorption energy

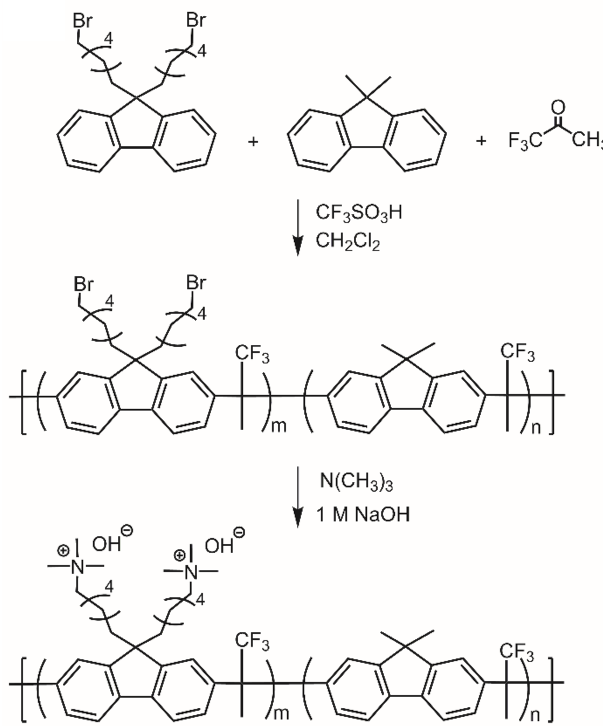
Pt-Ru

Biphenyl Adsorption energy **Fluorene**

- Fluroene-Pt/Ru interface has the least interaction which can minimize the interaction with HOR catalysts.

Down-selected Ionomer poly(fluorene)s (FLN)

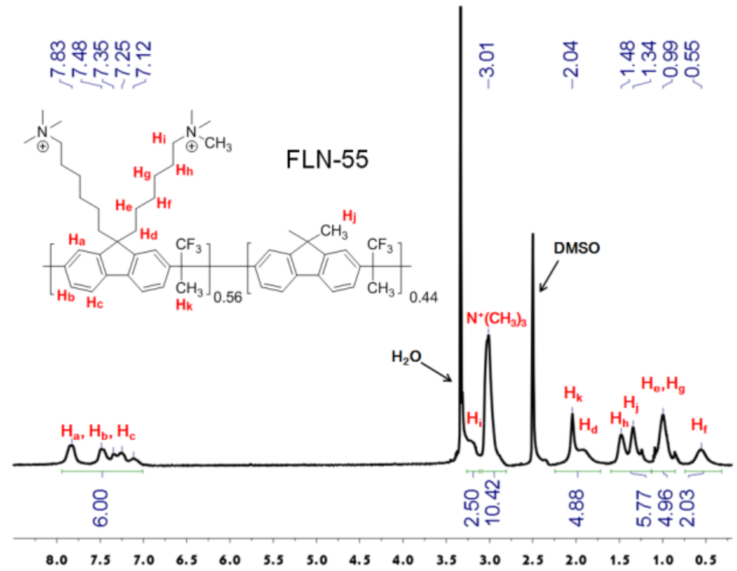
Synthetic Procedure of FLN



FLBr 30: m = 0.28, n = 0.72
FLBr 40: m = 0.38, n = 0.62
FLBr 55: m = 0.56, n = 0.44

FLN 30: IEC = 1.5 meq. g^{-1}
FLN 40: IEC = 2.0 meq. g^{-1}
FLN 55: IEC = 2.5 meq. g^{-1}

^1H NMR spectra of FLN (DMSO-d_6)



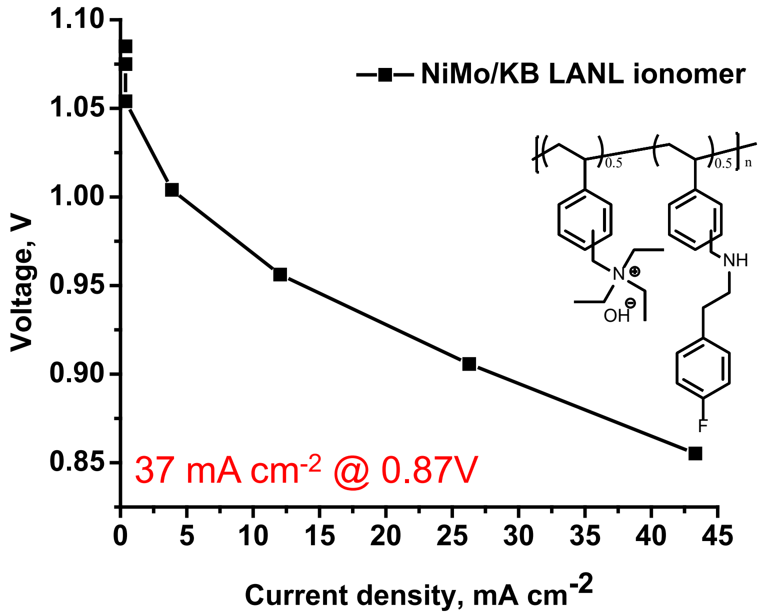
IEC (meq. g^{-1})			WU [a] (wt.%)	σ (mS cm^{-1})	
Theoretical	^1H NMR	titration		30 °C	80 °C
2.5	2.5	2.5	180	110	120

- Down-selection was based on alkaline stability and minimum interaction with catalysts

Preliminary Non-PGM catalyst works

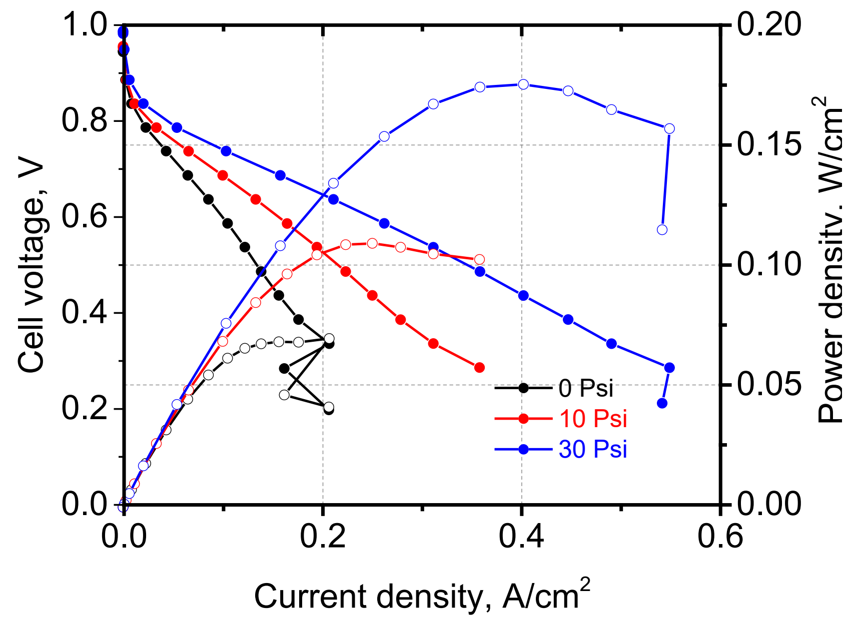
NiMo/C HOR catalyst (UNM)

AEM: Tokuyama A201, **Ionomer:** QASOH, **Catalyst:** NiMo/C 4 mg/cm^2 (anode), Pd/C 0.2 mg_{Pt}/cm^2 (cathode). Measured under H_2/O_2; 50kPa (gauge) backpressure



N-doped C ORR catalyst (WSU)

AEM: TPN, **Ionomer:** FLN, **Catalyst:** Pt-Ru/C 0.5 mg/cm-2 (anode), N-doped C 0.6 mg_{Pt}/cm^2 (cathode). Measured under H_2/O_2; various backpressure



- NiMo/C anode catalyzed MEA exhibited impressive kinetic performance (0.37 mA/cm^2 at 0.87 V; but anode was flooded at high current density.
- N-doped C catalyzed MEA exhibited relatively poor performance. Further investigation is on going.

Los Alamos NATIONAL LABORATORY THE UNIVERSITY OF NEW MEXICO WASHINGTON STATE UNIVERSITY